Title	Thermodynamic Analysis of Ammonia-Water-Carbon Dioxide Mixtures For Designing New Power Generation Cycles.
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Abstract

Objectives

The goal of this project is to develop a computational package for the prediction of thermodynamic properties (vapor-liquid equilibrium, specific heat, volume, bubble and dew points, solubility, corrosivity) for ammonia-water-carbon dioxide mixtures at high temperatures and pressures. This package will be used for the design and analysis of hybrid power cycles. The specific tasks are:

1. Review existing thermodynamic property data and prediction methods for ammonia-water-carbon dioxide mixtures.
2. Develop detailed nonideal thermodynamic property prediction subroutines for these mixtures.
3. Use of the above models to fit and predict properties for the mixtures.
4. Develop simplified thermodynamic models, in smaller pressure-temperature ranges, for use in optimization based analysis and synthesis of advanced power cycles.

Accomplishments To Date

We have progressed on two fronts in this study, each of which are described below:

- Thermodynamics for Ammonia-water-carbon dioxide mixtures, and
- Design and optimization of power cycles featuring these mixtures.

Thermodynamics: We initiated a review of thermodynamic data available on ammonia-water mixtures. We have also obtained a database from NIST, Boulder, CO from Dr. Daniel Friend, for NH_3-H_2O mixture data. Published thermodynamic property equations predict large deviations from experimental data at pressure and temperatures near the mixture critical point. A set of empirical equations of state for the *ammonia-water mixture* developed by Ibrahim and

Klein were modified for developing the prediction package. The predictions were compared with published experimental data, and the predictions agree very well for design purposes.

We modified the thermodynamic package to include *carbon dioxide* in the mixture. Its addition leads to reactions in the liquid phase. Our package calculates simultaneous reaction and phase equilibrium. The Wagner equation of state will be used for carbon-dioxide gas phase properties. In the liquid phase, ionic species and reactions are accounted for through the Pitzer's ionic model, as modified by Rumpf and Maurer. The significant challenge here is to find experimental data on this system that includes liquid phase molalities and species enthalpies.

Finally, thermodynamic computations above require solving a large set of nonlinear equations. Hence, the program is not suitable for optimization where thousands of function evaluations may be required. To enhance its speed and robustness, we have

- incorporated analytical gradients in the Newton solver for the routines, and
- developed a thermodynamically consistent linearized predictor for the stream property states (compositions, temperature, pressure, enthalpy, entropy, etc.) around a given state. This simplifies the optimization run. The validity of this fit is tested once the iteration converges, and this procedure is repeated for the solution.

Design of Power Cycles: We assessed the feasibility of using this complicated model with optimization routines for the design and analysis of the power cycle. An earlier version of our own Kalina cycle optimization code was modified to use this package. Both a deterministic optimizer, MINOS, and a stochastic one using differential evolution, a genetic algorithm based technique, were used.

We have now developed a new approach to the design and optimization of this cycle, where we represent the power cycle as a process graph that has input and output nodes (the stream states). Stream connect the input to the output nodes and undergo a transformation through a unit operation such as a heat exchanger or a turbine. This representation is then coded mathematically, and optimized for the stream flows. Rigorous, non-simplified thermodynamics can be incorporated here. The resulting problem is a large linear program that can be solved for its global solution. *This approach provides the first global utility cost bounds for mixed fluid bottoming power cycles.*

Significance To Fossil Energy Programs

Advanced power generation cycles, for *bottoming cycle* applications, have been proposed in the last decade that employ a mixture of *ammonia/water* and even *carbon-dioxide* instead of pure water as a working fluid in the cycle. *Efficiency improvements* of over 20% over conventional bottoming cycles are claimed for these cycles. Such power cycles will allow the efficient utilization of the nation's fossil reserves while reducing the emissions of greenhouse gases. Since these cycles are used in recovering heat from cogeneration turbines, they will form an integral part of DOE's Vision 21 advanced power coproduction facility.

Plans For The Coming Year

We plan to continue work on the optimization of the bottoming power cycles. We will also try to obtain better data for ammonia-water-carbon dioxide mixtures.

Presentations and Student Support

Journal Articles (Peer Reviewed)

Patra, A. and Gupta, A. "A Systematic Strategy For Simultaneous Adaptive *hp* Finite Element Mesh Modification Using Nonlinear Programming," *J. Applied Comp. Mech.*, Accepted.

Conference Presentations

- Gupta, A. and K.K.N. Sastry (Speaker), *A Graph Theoretic Approach To Power Cycle Synthesis.* Paper #219h. AIChE Annual Meeting, Dallas, FL, November 1999.
- Gupta, A. and K.K.N. Sastry, *Thermodynamic Models of Ammonia-Water-Carbon Dioxide Mixtures For Optimal Design of Hybrid Power Cycles.* Paper #87p. AIChE Annual Meeting, Dallas, FL, November 1999.
- Gupta, A. and A. Patra, *Adaptive hp Finite Element Mesh Modification Using Nonlinear Programming.* Paper #213b. AIChE Annual Meeting, Dallas, FL, November 1999.
- Gupta, A. (Invited) *A Graph Theoretic Approach To Hybrid Power Cycle Synthesis.* Department of Chemical Engineering, University of Notre Dame, South Bend, In, October 1999.
- Gupta, A. (Invited) *Synthesis of Hybrid Power Cycles.* NSF Workshop on Hybrid Technologies for Waste Minimization, Breckenridge, CO, July 1999.
- Gupta, A. and A. Patra, *A Systematic Strategy for Simultaneous Adaptive hp Finite Element Mesh Modification Using Nonlinear Programming.* Paper #MS29d. SIAM Annual Meeting, Atlanta, GA, May 1999.

Students Supported Under This Grant

- Kumara Narasimha K Sastry, graduate student, 1/1999-12/1999, in Chemical Engineering, University at Buffalo